[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

A Study of the Dilatometric Method of Measuring Rates of Reactions: The Application to the Determination of the Rate of Hydrolysis of Acetal

BY L. K. J. TONG AND A. R. OLSON

The dilatometer as well as the interferometer lend themselves very nicely to the study of rates of reaction if the sum of the partial volumes of the products differs from the sum of the partial volumes of the reactants. Care, however, must be exercised to exclude various heating effects such as the heat of solution and the heat of reaction. While some investigators like Luten[1] and Akerlöf[2] have concerned themselves with the problem, all too often these factors have been overlooked or dismissed as unimportant.

Applied to the hydrolysis of acetal, the problem can be visualized as follows. Let ΔH_s be the heat absorbed in calories per mole of acetal dissolved and ΔH be the heat absorbed due to the hydrolysis of acetal in calories per mole. If the dissolution takes place so quickly that we can neglect any flow of heat through the dilatometer walls in that time, then $T_0 - T' = -\Delta H_s x_0/C_p$, where T_0 is the effective temperature inside the dilatometer, T' is the temperature of the thermostat, x_0 the number of moles of substrate dissolved and C_p is the heat capacity of the dilatometer system. After some time interval, dt, dx moles will have hydrolyzed, absorbing $\Delta H dx$ calories of heat. During the same time interval $f(T - T')dt$ calories will flow through the dilatometer boundaries where T is the effective temperature inside the dilatometer at the time t, and f is Newton's transmission coefficient, and so

$$C_p \frac{dT}{dt} = +\Delta H \frac{dx}{dt} - f(T - T') \qquad (1)$$

For a reaction of the first order

$$dx/dt = -kx_0 e^{-kt} \qquad (2)$$

where k is the specific reaction rate. Substituting this into (1) and integrating, we obtain

$$T - T' = -\frac{\Delta H k x_0 e^{-kt}}{C_p\left(\frac{f}{C_p} - k\right)} + Ce^{-ft/C_p} \qquad (3)$$

When $t = 0$

$$\frac{-\Delta H_s x_0}{C_p} = -\frac{\Delta H k x_0}{C_p\left(\frac{f}{C_p} - k\right)} + C \qquad (4)$$

and so

$$T - T' = -\frac{x_0}{C_p}\left[\frac{\Delta H k}{\left(\frac{f}{C_p} - k\right)}(e^{-kt} - e^{-ft/C_p}) + \Delta H_s e^{-ft/C_p}\right] \qquad (5)$$

an equation which is essentially the same as that obtained by Luten. If v is the volume of the dilatometer, r, the radius of the dilatometer capillary, and α the temperature coefficient of expansion, then the difference in meniscus level from that at thermal equilibrium, $h - h'$, is given by

$$h - h' = \frac{-\alpha v x_0}{\pi r^2 C_p}\left[\frac{\Delta H k}{\left(\frac{f}{C_p} - k\right)}(e^{-kt} - e^{-ft/C_p}) + \Delta H_s e^{-ft/C_p}\right] \qquad (6)$$

which involves only experimentally determinable quantities.

In Fig. 1 we show the diagram of the dilatometer which we used to determine the rate of hydrolysis of acetal. The stopcock between the two bulbs was fitted with a long handle so that it extended above the thermostat liquid. The dilatometer bulb was fitted with a glass-enclosed piece of iron (C) for magnetic stirring.

The thermostat was controlled by a toluene regulator. For a change in temperature of a hundredth of a degree the mercury in the regulator travelled 1.1 cm. while the meniscus in the dilatometer capillary changed 0.26 cm. and so the temperature regulation was sufficient for our purpose.

The chemicals were of the best reagent quality. Except for the acetal they were not purified further. The acetal was stored first over calcium chloride and then over solid sodium hydroxide. The decanted liquid was then fractionated at low pressure in a meter-long column. Its boiling point was 67.3 ± 0.05 at 22.2 cm.

In making a run, the solvent was placed in bulb A and left there until it came to the thermostat temperature. The acetal (about 0.2 cc.) was then added from a pipet and the solution stirred thoroughly with a bent glass rod. The stopcock between the bulbs was then opened and the liquid forced into bulb B by applying compressed air to A. After closing the stopcock securely, the reaction was followed by observing the height of the meniscus in the capillary D at various times.

In Fig. 2 we have plotted $(h_\infty - h)$ against time for the latter portion of two runs. In the run marked "a" we stirred the solution whereas in run "b," no stirring was used. The discrepancy between "a" and "b" showed that the heat of solution or the heat of reaction or both had

(1) Luten, *J. Phys. Chem.*, **39**, 199 (1935).
(2) Akerlöf, THIS JOURNAL, **49**, 2955 (1927).

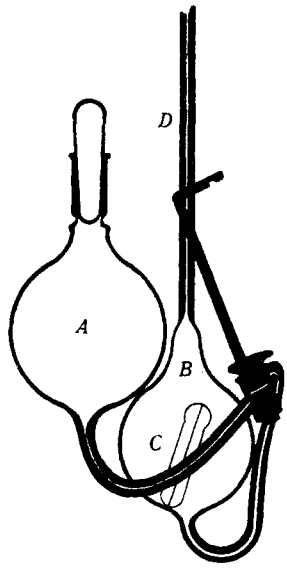

Fig. 1.—Dilatometer: A, mixing bulb; B, reaction bulb; C, glass-enclosed magnetic stirrer; D, capillary 0.47 mm. diameter.

introduced considerable error in the determination of the rate constant, and so we determined next the magnitude of these heat effects.

The calorimeter for determining the heats consisted merely of a half-gallon Dewar flask fitted with a Beckmann thermometer, a stirrer and a pipet (for introducing the acetal), the lower part of which was bent in the form of a gooseneck. The calorimeter was kept in a small room which was thermostated to 25 ± 0.1°.

The heat capacity of the system was calculated from the observed temperature change when a two-gram piece of ice was added to the 1500 cc. of water in the flask. It was checked by adding 2 cc. of 6 N sulfuric acid to the calorimeter and calculating the heat from the temperature change and the known heat of dilution of sulfuric acid.

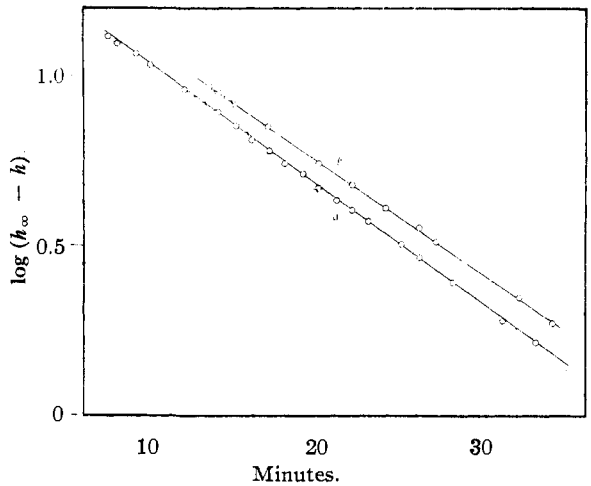

Fig. 2.—Rate of hydrolysis of acetal in 10^{-3} m./l. HCl: (a) with stirring; (b) without stirring.

The heat of solution was then determined by filling the pipet with acetal, placing it in the calorimeter water and leaving it there until the thermometer showed only a small linear drift with time—the gooseneck and the small aperture permitting only a very small amount of mixing. The acetal was then forced into the water by applying a slight air pressure to the pipet, taking care not to blow air into or onto the water. The amount of acetal transferred was obtained from an analysis of the final solution. Temperature readings again were taken until a linear change with time was obtained. From the linear extrapolations of these sets of readings, the heat evolved per mole of acetal dissolved in water at 25° was found to be 4,700 calories. From the solubility of acetal in 4 M sodium chloride solution at 0° and at 25°, we find that the heat of solution corresponds to evolution of +4250 calories. Similar calculations for 1 M potassium nitrate solutions give 5560 calories per mole.

The heat of hydrolysis was then determined by adding a small amount of sulfuric acid to the acetal solution in the calorimeter, and again observing the temperature. Again correcting for the heat of dilution of the sulfuric acid we find that in water the heat of hydrolysis of acetal at 25° corresponds to an absorption of 4100 calories per mole, in 4 M sodium chloride solution to 5100 calories per mole, and in 1 M potassium nitrate solution to 4500 calories per mole.

The cooling constant of the dilatometer was obtained in the following manner. After some of the rate runs were completed, the dilatometer was removed from the thermostat for a short time (one-half min. to one min.) to permit it to cool slightly. It was then replaced and a series of meniscus readings were taken as the final value in the corresponding rate run was approached asymptotically. In the plot of ln (h − h') against time, a straight line was obtained as shown in Fig. 3. The slope of this line was taken as f/C_p.

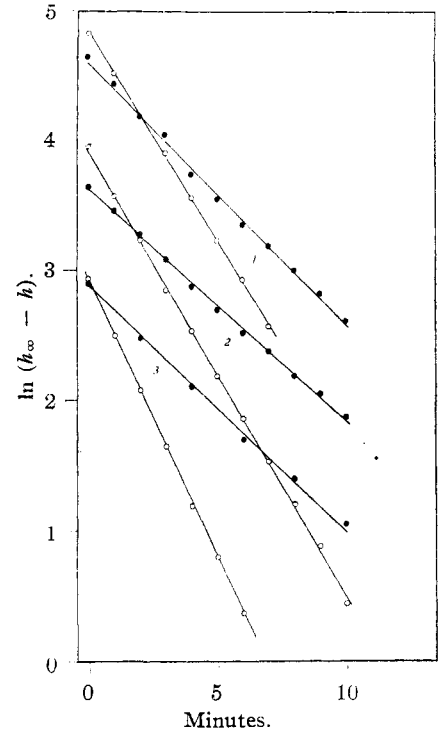

Fig. 3.—Rates of heat transfer through the wall of dilatometer: 1, water; 2, 4 m./l. NaCl; 3, 1 m./l. KNO_3; open circles with stirring; closed circles without stirring.

The thermal coefficient of expansion was measured directly by changing the temperature of the thermostat. c_p's for the solvents were taken from "I. C. T." The data are summarized in Table I.

TABLE I

	Water	4 *M* NaCl	1 *M* KNO_3
ΔH solution	−4,700	−4,250	−5,560
ΔH hydrolysis	4,100	5,100	4,500
$h_\infty - h$, cm./millimole reacted	3.70	4.1	3.8
α, cm./°C.	26.0	40.8	36.0
f/C_p (with stirring)	0.33	0.35	0.43
f/C_p (without stirring)	.20	.18	.18
c_p/g. solution	1.00	.815	.900

In Fig. 4, curve A, we have plotted the change in the meniscus level which we should observe if there were no heat effects, for the hydrolysis of 0.01 mole of acetal in 154 cc. of 4 *M* sodium chloride and which has a sufficient concentration of hydrogen ion so that $k = 0.100$ min.$^{-1}$. In this plot we have used the experimentally determined volume change for the reaction. In curves B and C, we have plotted the meniscus changes due to the heat effects alone, where for $t = 0$ we have taken the time when the acetal had just dissolved. For curve B we used the cooling constant of the stirred solution, and for curve C that of the unstirred solution. In an actual run we observe the resultant of both changes.

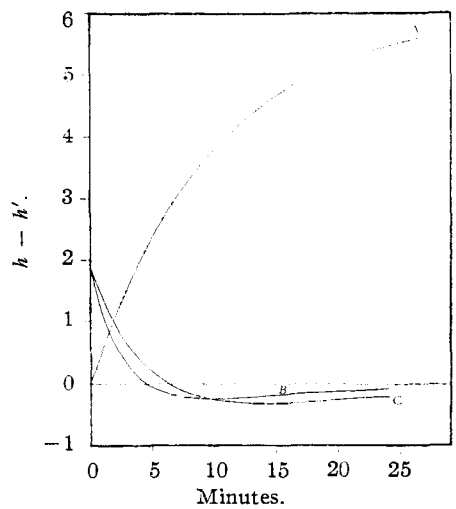

Fig. 4.—Calculated volume changes in 4 m./l. NaCl solution: (a) due to volume change at constant temperature $k = 0.100$ min.$^{-1}$; (b) due to temperature effects with stirring, assuming no volume change due to the reaction; (c) due to temperature effects without stirring, assuming no volume change due to the reaction; h' is the initial position of the meniscus at equilibrium temperature.

In Fig. 5 we have plotted ln $(h_\infty - h)$ against the time. Curve 3 corresponds to curve A in Fig. 4. Curve 2 is that which we calculate from the sum of curves A and B in Fig. 4, *i. e.*, what we should observe in an actual run with stirring, and curve 1 is obtained from curves A and C in Fig. 4.

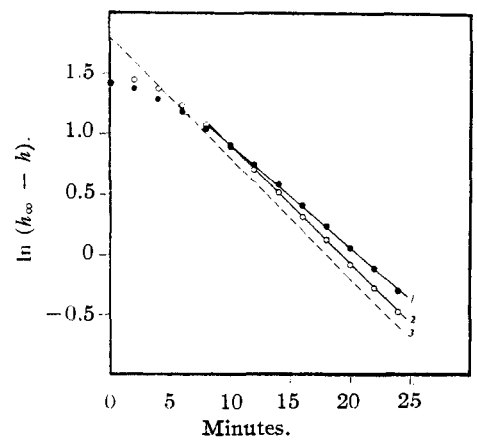

Fig. 5.—1, Apparent slope without stirring; 2, apparent slope with stirring; 3, theoretical slope without temperature effect.

Ignoring the points obtained during the first ten minutes of the reaction, which permits the heat

TABLE II

Author	C_{H^+}	C_{acetal}	t, °C., measured	k_{H^+} at t, °C.	k_{H^+} 25° calculated
		Bisulfite titration			
Skrabal[4] and Mirtl			25	50, 56, 80	50, 56, 80
Palomaa and Aalto[5]	0.00113	0.0870	25	68.5	68.5
Brønsted and Wynne-Jones[3]	.001	.03- .08	20	44.2	84.0
		Dilatometer			
Palomaa and Solonen[6]	.001	.2	25.0	76.5	76.5
Kilpatrick and Chase[7]			0	2.40	76.0
Riesch and Kilpatrick[8]			0	2.46	82.0
Tong and Olson	.0010	.01	24.89	76.9	78 not stirred
				81.0	82 stirred
		Interferometer			
Hornel and Butler[9]	.001		15.0	19.0	70.4

(3) J. H. Brønsted and Wynne-Jones, *Trans. Faraday Soc.*, **25**, 59 (1929).
(4) Skrabal and Mirtl, *Z. physik. Chem.*, **111**, 98 (1924).
(5) Palomaa and Aalto, *Ber.*, **66**, 468 (1933).
(6) Palomaa and Solonen, *ibid.*, **67**, 424 (1934).
(7) Kilpatrick and Chase, THIS JOURNAL, **53**, 1732 (1931).
(8) Riesch and Kilpatrick, *J. Phys. Chem.*, **39**, 561 (1935).
(9) Hornel and Butler, *J. Chem. Soc.*, 1361 (1936).

of solution to be dissipated, and drawing straight lines through the remaining points, we find that a value of k determined from curve 2 is 2% low and a value of k determined from curve 1 is 15% low.

Since the magnitude of the error depends upon the velocity of the reaction, it seems not improbable that this might account for the trend which Brønsted and Wynne-Jones[3] observed as they varied the concentration of the hydrogen ion. Their assumption that the trend was due to oxidation of the acetal would require an amount of acid to be produced which seems quite unlikely.

In Table II we summarize the various determinations of the hydrogen ion catalyzed rate constant for the hydrolysis of acetal in water. If the experiments were not done at 25°, the rate at this temperature was calculated using the heat of activation as determined by Kilpatrick and his students.

Summary

We have analyzed the effects of the heat of solution and the heat of reaction on the determination of rate constants by the dilatometric method.

We have devised a magnetically stirred dilatometer which minimizes the errors due to these effects.

We have determined the heat of solution and the heat of hydrolysis of acetal in water, in 4 M sodium chloride and in 1 M potassium nitrate, and also the volume change due to hydrolysis in these systems.

We have also determined the hydrogen ion catalyzed rate constant for the reaction in these solvents at 25°.

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The Configuration of Starch in the Starch–Iodine Complex. III. X-Ray Diffraction Studies of the Starch–Iodine Complex[1]

BY R. E. RUNDLE AND DEXTER FRENCH

Introduction

In two previous papers[2] optical evidence has been presented that under certain conditions starch chains possess a helical configuration. The modifications which have been examined and which appear to have this configuration are: (1) the "V"[3] modification of starch, *i. e.*, starch precipitated with certain alcohols, and (2) the starch–iodine complex, where the starch helices appear to contain the iodine molecules, as in Fig. 1 of (a).[2] On the other hand, in granular and retrograded starches the starch chains appear to be extended into some essentially linear configuration.[4] Earlier work on the helical configuration is reviewed briefly in the previous papers.[2]

Reported here is an investigation of the starch–iodine complex by X-ray diffraction. This work provides important confirmatory evidence for the structure previously proposed for the starch–iodine complex; moreover, it suggests certain additional features of the structure.

Preparation of the Starch–Iodine Complex.—Recently, Schoch's[5] fractionation of starch has made available the amylose component of starch.[6] In this component the regularities of the starch chains are not interrupted by frequent branching.[2,5,7] As a result, all the crystalline modifications of the amylose component are superior to those same crystalline modifications for whole starch.[8] All iodine complexes used in this investigation were prepared from amylose.

The starch–iodine complex or, more strictly, the amylose–iodine complex was prepared by

(1) Journal Paper No. J-1106 of the Iowa Agricultural Experiment Station, Ames, Iowa, Project No. 639. Supported in part by a grant from the Corn Industries Research Foundation.

(2) (a) R. Rundle and R. Baldwin, THIS JOURNAL, **65**, 554 (1943); (b) R. Rundle and D. French, *ibid.*, **65**, 558 (1943).

(3) Starch exists in several crystalline modifications. Classification can be made on the basis of X-ray diffraction patterns. For nomenclature see J. Katz and T. van Itallie, *Z. physik. Chem.*, **A150**, 90 (1930); also, J. Katz and J. Derksen, *ibid.*, **A167**, 129 (1933).

(4) (a) R. S. Bear and D. French, THIS JOURNAL, **63**, 2298 (1941); (b) A Frey-Wyssling, *Naturwissenschaften*, **28**, 78 (1940); *Ber. schweiz. botan. Ges.*, **59**, 321 (1940).

(5) T. J. Schoch, THIS JOURNAL, **64**, 2957 (1942).

(6) In this paper we shall adopt the nomenclature of K. Meyer, "Rev. Colloid Science," Interscience Pub., Inc., New York, N. Y., p. 142. The unbranched component of starch will be referred to as "amylose."

(7) F. L. Bates, D. French and R. Rundle, THIS JOURNAL, **65**, 142 (1943).

(8) It is a point of importance that the amylose component in its various modifications gives the same diffraction patterns as whole starch. This observation would require that all points of branching be interruptions in the crystalline structure of starch. A critical examination of this observation will be reported in a subsequent paper.